HOMOGENEOUS KINETICS OF THE REACTION OF CARBONDIOXIDE AND DIETHANOLAMINE BY STOPPED FLOW METHOD

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By

P. V. RAO

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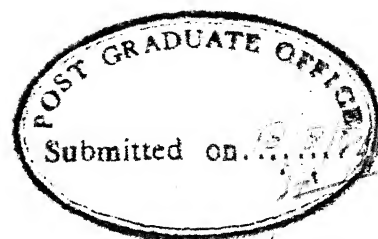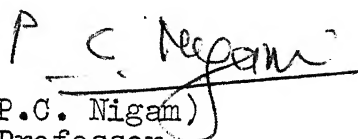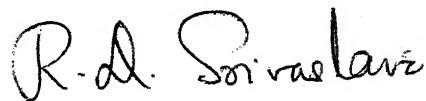CHE-1984-M-RAO-HOM

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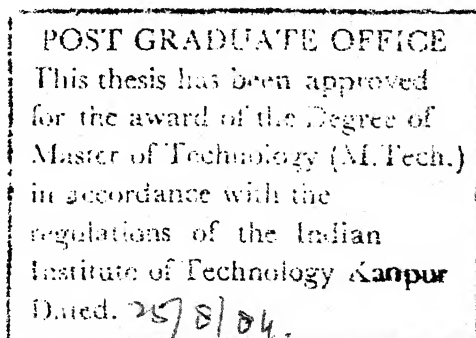

(P.C. Nigam)
Professor
Department of Chemistry
Indian Institute of Technology
Kanpur-208016, India

August 18, 1984

(R.D. Srivastava)
Professor
Department of Chemical Engineering
Indian Institute of Technology
Kanpur-208016, India

August 18, 1984

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ABSTRACT

The kinetics of the homogeneous reaction of carbon dioxide with diethanolamine (DEA) have been investigated using the stopped flow method with optical detection in the concentration range $[DEA] = 0.07 - 0.10$ M and $[CO_2] = 5.36 \times 10^{-3}$ M. The study indicates that overall reaction is second order, (i.e.), first order both in carbon dioxide and diethanolamine. The second order rate constant was found to be 26 ± 2 lit/gmole sec at 298 K. The activation energy was calculated as 43.6 KJ/mole.

The pH dependence of rate constant was studied in order to determine the effect of hydrogen ion concentration on CO_2-DEA reaction. A mechanism which is in consistent with the experimental results has been proposed. Individual rate constants for pairs of reactive species present in the system were calculated using pH dependence.

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NOMENCLATURE

k_2 Second order rate constant, lit/gmole sec.

t Time, sec.

V_t Transmitted light intensity at time t, volts

V_o Transmitted light intensity with a non absorbing sample, volts

V_{io} Transmitted light intensity at infinite time, volts

D_t Optical density

G_t Number of voltage graduations at time, t

E_{act} Energy of activation, KJ/mole

R (C_2H_4OH) group

$[DEA]$ Initial total DEA concentration, M

$[CO_2]$ Initial total CO_2 concentration, M

$[Ind]$ Initial indicator concentration, M

k_{obs} First order observed rate constant, sec^{-1}

T Temperature, K

$k_{Am, free}^{CO_2, free}$ Rate constant for the reaction between $CO_{2,free}$ and $Am_{,free}$ species, lit/gmole sec.

$k_{AmH^+}^{CO_2, free}$ Rate constant for reaction between $CO_{2,free}$ and AmH^+ species, lit/gmole sec.

$k_{Am, free}^{HCO_3^-}$ Rate constant for reaction between HCO_3^- and $Am, free$ species, lit/gmole sec.

$k_{AmH^+}^{HCO_3^-}$ Rate constant for reaction between HCO_3^- and AmH^+ species, lit/gmole sec.

$k_{Am,free}^{CO_3^{--}}$ Rate constant for reaction between CO_3^{--} and Am,free species, lit/gmole sec.

$k_{AmH^+}^{CO_3^{--}}$ Rate constant for reaction between CO_3^{--} and AmH^+ species, lit/gmole sec.

CHAPTER 1

INTRODUCTION

1.1 General:

The reactions of carbon dioxide with amines are of industrial and biological significance. Aqueous solution of diethanolamine (DEA) is used as a powerful and rapid absorbing agent for removal of both carbon dioxide and hydrogen sulfide. DEA is the most preferred absorbing agent in industrial processes because of its low volatility, low corrosiveness, high reactivity, thermal stability and ease in regeneration of absorbing solution. In the biological context, enzymes containing metal bound amino groups play an important part in the transport of carbon dioxide from the blood stream.

In most practical situations, the rate of absorption is influenced by the kinetics of the reaction between carbon dioxide and diethanolamine solution. Therefore, a knowledge of the kinetics of the reaction between carbon dioxide and DEA solution is very important in the rational design of absorption equipment. Although, the kinetics of this system (CO_2 removal by DEA) have been investigated by many workers, considerable discrepancies exist for this reaction between various experimental results. It has been recently pointed out [1,2] that the main reason for this disagreement is the fact that the reaction mechanism is far more complicated than most authors assumed.

It is essentially in regard to this point, the present work was carried out to clarify the kinetics and mechanism of $DEA-CO_2$ reaction. In this kinetic investigation, increased emphasis has been placed on the parametric dependence of the pH of the reacting medium upon the reaction rate.

1.2 Literature Survey:

The earliest study of the reaction between CO_2 and DEA was conducted by Jensen, Jorgensen and Fourholt [3]. Atmospheric air containing about 10 percent CO_2 was led into solutions containing both amine and sodium hydroxide. The concentration of sodium hydroxide was varied from half to double the amine concentration. These authors observed that carbamate was the only reaction product and it decomposed to carbonate after several minutes. The second order rate constant reported at 291 K was 5400 lit/gmol sec. Jorgensen [4] studied the CO_2-DEA system using the same experimental technique as Jensen et al. [3] and also obtained a value for carbamate formation of 5400 lit/gmol sec at 291 K. However, Jorgensen [4] allowed the possibility of a competing reaction indicating that the reaction product formed was a mixture of carbamate and alkyle carbonate. In strongly alkaline solutions, the amount of alkyle carbonate formed was excessive. Sodium hydroxide concentration was varied from one third to three times the DEA concentration.

Nunge and Gill [5] studied the absorption of CO_2 into
pure DEA in a gas-liquid stirred reactor at 302, 308, and 314 K.
The absorption was followed by pressure-time measurements. An
equation describing the gas-liquid absorption system was
derived and then simplified by considering only kinetic region.
The experimental data were correlated with this simplified
equation and they indicated that the reaction follows a third
order equation, i.e. first order in CO_2 and second order in
DEA.

Sharma [6] studied the reaction between CO_2 and DEA, and
suggested that the reaction takes place according to the following
mechanism:

$$CO_2 + R_2NH \longrightarrow R_2NCOO^- + H^+ \tag{1}$$

$$H^+ + R_2NH \longrightarrow R_2NH_2^+ \tag{2}$$

$$CO_2 + 2R_2NH \longrightarrow R_2NH_2^+ + R_2NCOO^- \tag{3}$$
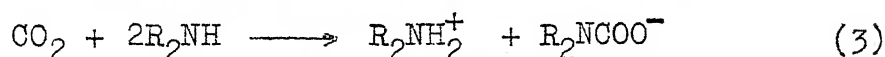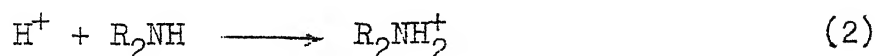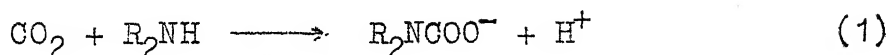
in which the first step reaction Eq.(1) is second order, (i.e.),
first order with respect to both CO_2 and DEA, and is rate
controlling [7]. The R in (1) to (3) is C_2H_4OH group. The
reaction proceeded to give amine salt of carbamic acid as the
product of the reaction. The second order rate constant was
found to be 1000 lit/g mol sec at 291 K. Sharma [6] also
reported that the contributions of the reactions with water
and hydroxyl to the overall rate of reaction were negligible

under conditions used in practice for absorption of CO_2 in aqueous DEA solutions.

Leder [8] studied the absorption of CO_2 in potassium carbonate-bicarbonate buffer solutions at higher temperatures. The rates of absorption were catalyzed by adding small amounts of water-soluble amines. The second order rate constant for CO_2-DEA system was found to be 5556 lit/gmole sec at 292 K. The activation energy was calculated to be 43.9 KJ/gmole.

Hikita et al.[9] used rapid mixing method to study the kinetics of reaction of CO_2 with DEA. The overall reaction was observed to be of third order, i.e., first order with respect to CO_2 and second order with respect to DEA. The experiments were conducted for short contact times (maximum of about 20 milli sec.). A constant heat of reaction was assumed without knowing its value either experimentally or from literature. The activation energy was found to be 53 KJ/gmole.

Sada et al.[10] carried out experiments over a wide range of contact times for the absorption of CO_2 into aqueous amine solutions. It was suggested from the experimental results with a laminar liquid jet, a wetted wall column and a quiescent liquid absorber that the present absorption processes should be analysed by a gas absorption with the consecutive reaction of the form of $A + 2B \xrightarrow{k_I} R$ and $A + R \xrightarrow{k_{II}}$ products. The value of the second order rate constant for the first reaction step (k_I) was estimated as 1340 lit/gmole sec at 298 K.

The k_{II} was estimated as 6.7×10^{-2} lit/g mole sec at 298 K.

Coldrey and Harris [11] studied the kinetics of the liquid phase reaction between CO_2 and DEA by flow thermal method. The data indicated that the kinetics of the reaction is complex. The particular mechanism proposed consisted of two reactions with initially complete for the available CO_2. One of these reactions was reversible and regenerated CO_2 as the overall reaction proceeded. Following is the reaction scheme proposed by these authors.

$$CO_2 + 2\,R_2NH \xrightarrow{\;\;k_1\;\;} R_2NCOO^- + R_2NH_2^+ \qquad (4)$$

$$CO_2 + 2\,R_2NH \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \text{Products} \qquad (5)$$
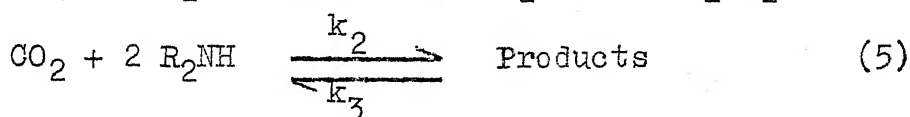
The species participating in the proposed reversible reaction (5) were not identifiable from the data obtained. Apparent heat of reaction was also measured experimentally and it was found that it varied with the DEA concentration in the solution. The value of k_1 was obtained as 800 lit/g mole sec at 291 K and 48.7 KJ/g mole apparent heat of reaction.

Donaldson et al. [12] found the reaction kinetics of CO_2-DEA reaction using a tracer CO_2 membrane transport technique[13, 14, 15]. They conducted experiments with membrane containing 0.031 to 0.088 M DEA. They reported a second order rate constant for carbamate formation at 298 K as 400 lit/g mole sec for high concentrations and 1400 lit/g mole sec for low concentrations.

Alvarez-Fuster et al. [16] studied CO_2-DEA reaction using a wetted wall tower, in the concentration range of 0.25 - 0.82 M DEA. They reported an overall third order reaction, i.e., second order with respect to DEA. They reported a third order rate constant of 840 lit^2/g-mole^2 sec.

Laddha et al. [17] investigated CO_2-DEA reaction using a stirred vessel. They observed that presence of K_2CO_3 in DEA solution increases the rate of reaction. They have reported a correlation, for second order rate constant for CO_2-DEA reaction. Blauwhoff et al. [2] studied the reaction between CO_2 and DEA, using a stirred vessel similar to that of Laddha et al. [17]. They reported an overall second order rate constant of 4100 lit/gmole sec at 298 K in the DEA concentration range of 0.393 - 2.308 M.

Recently Barth et al.[18] studied the CO_2 reaction with DEA, using stopped flow method with optical detection in the ranges of 0.111 - 0.084 M DEA and 2.94 - 5.6 x 10^{-3} M CO_2 concentrations. A first order reaction relative to DEA was found with a rate constant for carbamate formation, as 110 $\pm$ 15 lit/gmole sec at 298 K. The equilibrium constant for the same reaction was also determined giving pK_R = 5.3 at 298 K. They proposed the following mechanism, in which the carbamate formation takes place simultaneously with the hydration reactions.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \tag{6}$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \tag{7}$$

$$CO_2 + R_2NH \rightleftharpoons R_2NCOO^- + H^+ \tag{8}$$
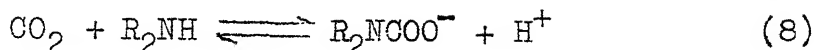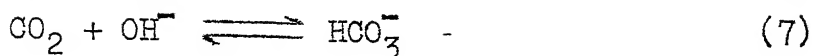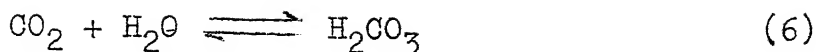
When $[DEA]/[CO_2] \gg 2$, reaction (8) was considered as completely displaced towards the formation of carbamate and thus treated as irreversible. These authors did not study the variation of rate constant with pH. Their mechanism seems to be incomplete, as reactions (6) and (7) would have occurred before the actual run in homogeneous liquid phase. The stoichiometry of the overall CO_2-DEA reaction is one to two of CO_2 and DEA, which enables the formation of protonated amine, as an end product. This step has not been included in the mechanism of this reaction.

Literature sources with kinetic data on aqueous DEA-CO_2 reaction are summarized in Table 1. The survey revealed that most kinetic studies of CO_2-DEA reaction were made by absorbing gaseous CO_2 directly into amine. Despite a considerable absorption data that exists for DEA, most investigations of the kinetics resulted in conflicting conclusions. The results of [5,9,16] differ greatly from others [2,10,11,17,18]. Serious discrepancies exist both in the reaction order and reaction rate constant values.

TABLE 1: LITERATURE DATA ON THE REACTION BETWEEN CO_2 AND AQUEOUS DEA

Reference	Temperature (range) K	DEA Conc. gmole/lit	$k_2 = \dfrac{r}{[CO_2]}$ Sec^{-1}	E_{act} Kj/mole	Experimental technique
Hikita et al. [9]	278.8–313.3	0.174–0.179	$10^{(12.41-\frac{2775}{T})} \times [DEA]^2$	53.1	Rapid mixing method
Nunge and Gill [5]	302.4–313.3	10–12	$C\ [DEA]^2$	54.4	Agitated vessel
Jørgensen [4]	273	0.1,0.2,0.3	$\dfrac{(730+4910\,[OH^-])[DEA]}{(692+3380\,[OH^-]+1056[DEA])}$ [DEA][16]	–	Competitive reaction with 0.1, 0.2, 0.3 M NaOH
Laddha and Danckwerts [20]	284	0.5–2.0	$\dfrac{[DEA]}{\frac{1}{890}+\frac{1}{560[DEA]}}$	–	Stirred cell
Jensen et al. [3]	291	0.1, 0.2	$5080\ [DEA]$	–	Competitive reaction with 0.1, 0.2 M NaOH
Jørgensen [4]	291	0.1,0.2,0.3	$(3990+13950[OH^-])[DEA]$	–	Competitive reaction with 0.1,0.2,0.3M NaOH
Sharma [21]	291	1.0	$1000\ [DEA]$	41.8	Laminar jet
Coldrey and Harris [11]	292	0.1–1.0	$430\ [DEA]+1000[OH^-]^{1/2}-$ $60([DEA]+[Product])/$ $[DEA][CO_2]$	48.7	Rapid mixing method with 0.002–0.005 M NaOH
Alvarez-Fuster et al. [16]	293	0.25–0.82	$840\ [DEA]^2$	–	Wetted wall column
Blanc and Demarais [22]	293–333	0.05–4.0	$10^{(-\frac{2274.5}{T}+10.4493)}[DEA]$	–	Wetted wall column
Ratkovics and Horvath [23]	293	0.108–0.964	$K_\alpha\ [DEA]^\alpha$	–	Packed column
Donaldson and Nguyen [12]	298	0.031–0.088	$1400\ [DEA]$ for [DEA] 0	–	Facilitated transport in aqueous amine membranes
Groothuis [24]	298	2.0	$1300\ [DEA]$	–	Stirred cell
Laddha and Danckwerts [25]	298	0.46–2.88	$\dfrac{[DEA]}{\frac{1}{1410}+\frac{1}{1200[DEA]}}$	–	Stirred cell
Sada et al. [10]	298	0.249–1.922	$1340\ [DEA]$	–	Laminar jet
Sharma [7,21]	298	1.0	$1500\ [DEA]$	41.8	L
Sharma [7,21]	308	1.0	$2500\ [DEA]$	41.8	l
Leder [8]	353	–	$1.78 \times 10^5\ [DEA]$	43.9	S
Blauwhoff et al. [2]	298	0.393–2.308	$(5.34[H_2O][DEA])+(7.05\times10^4$ $[OH^-][DEA])+228[DEA]^2$	–	Stirred cell
Barth et al. [18]	298	0.111–0.084	$110\pm15\ [DEA]$	–	Stopped flow

1.3 Present Work:

The objective of the present work has therefore been to study the kinetics of homogeneous liquid phase reaction between CO_2 and DEA by means of stopped flow method. Mechanism of this reaction was studied using pH variations in the reaction.

Since neither CO_2 nor DEA absorb in the UV or visible region our technique was to add a small amount of a pH indicator to monitor the concentration changes occurring within the mixing cell.

CHAPTER 2

EXPERIMENTAL APPARATUS AND PROCEDURE

2.1 Materials:

The prime materials used were diethanolamine (DEA) and carbon dioxide gas. DEA was obtained from Amines and Chemicals Limited, Bombay.

2.2 Principle of Stopped Flow:

The experimental method, known as stopped flow spectro-photometry, is used to determine the kinetics and rates of reactions, which result from the mixing of two samples A and B. These samples are contained in two syringes which are driven by a simple piston mechanism. The solutions therefore leave the two syringes with equal flow velocities and enter a mixing cell, where the mixing occurs and the following reaction starts:

$$A + B \longrightarrow C + D \qquad (9)$$
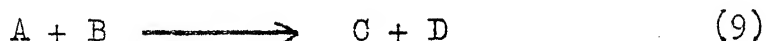
The mixed solution in which the reaction occurred, then enters a third syringe, the piston of which is driven back until it hits a stop which arrests the flow abruptly. The change in concentration of products is monitored continuously at the mixing cell.

2.3 Experimental Apparatus:

Stopped flow spectrometer, Nortech Lab., England (Model SF-3A), was used to follow the reaction between DEA and CO_2. The full apparatus is shown in Figure 1. The SF-3A apparatus consists of a flow unit, a control unit and an oscilloscope. These units are linked by light guides. The flow unit consists of two driving syringes, which hold the reactant solutions; the three-way stopcocks, used to fill these syringes or open them on to the flow circuit; the reactant reservoirs which hold the spare solutions of reactants and the mixing cell set underneath a thermostatic bath. Flow unit also contains a stopping syringe with a three-way stop-cock. The light guides, which carry the light beam, are used to monitor the concentration of products with time, at the mixing cell.

The control unit contains a deuterium light source, which is in connection with a monochromater, which has a wavelength setter. This control unit has a photomultiplier, that converts the light into voltage signal and sends it to oscilloscope. This control unit also has required controls to light source and the oscilloscope, such as bias, filter etc. The oscilloscope is triggered by a voltage pulse produced, when the piston of the stopping syringe strikes a microswitch on the stopping block. The controls for the visual display of output signal are provided with the oscilloscope.
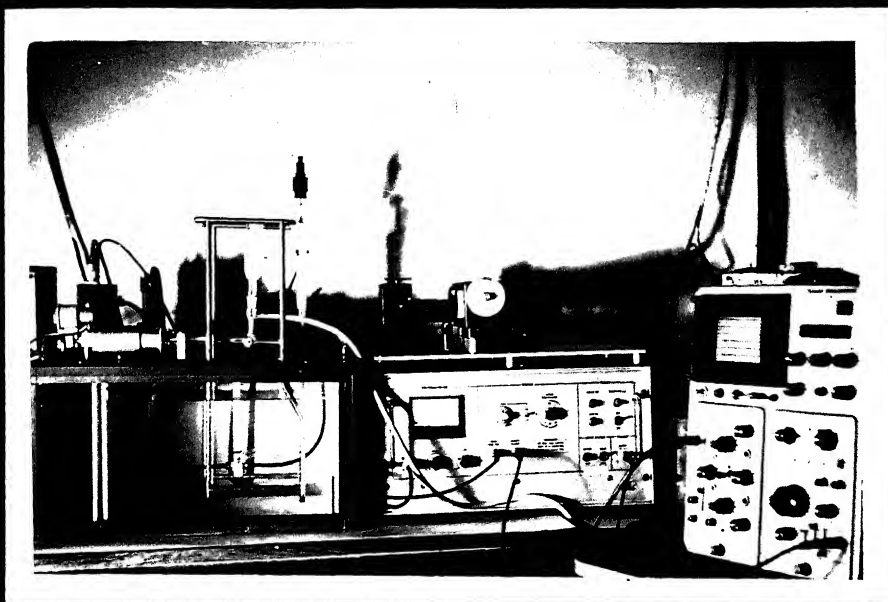
Fig.1 Stopped flow apparatus

2.4 Indicator Technique:

Since neither CO_2 nor DEA absorb radiation in the visible range of the electromagnetic spectrum, it was necessary to monitor concentration changes using an indicator technique[25]. DEA reacts with CO_2 according to the following overall stoichiometry.

$$2 \ R_2NH + CO_2 \rightleftharpoons R_2NCOO^- + R_2NH_2^+ \qquad (10)$$
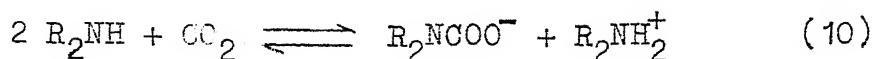
Protons are transferred to unreacted amine either via a zwitterionic intermediate or subsequent to the dissociation of an initially formed carbamic acid. In either case a proportion of these protons can be used to produce a color change in an indicator.

$$Ind + H^+ \rightleftharpoons Ind \ H^+ \qquad (11)$$

Calibration experiments carried out by adding known amount of CO_2 or hydrogen ions to indicator + amines solutions showed that concentration changes are directly proportional to optical density changes, for small changes in pH [25]. Provided therefore that the proton transfer to the indicator is rapid, the change in indicator concentration can be used to monitor the CO_2 reaction rate. Since many proton transfers in acid-base reactions approach diffusion controlled rates, this assumption is probably valid.

Indicators were chosen so that their dissociation constants were close to the hydrogen ion concentration at which

the reaction was studied. For this condition the acid and base forms of the indicator have equal concentrations and a given change in the hydrogen ion concentration brings about the largest change in optical density. In addition indicators with high molar extinction coefficients and with only one colored form were preferred. Table 2 lists the indicators used.

TABLE 2: INDICATORS

Indicator	pH range	Monitoring wavelength nm	Color change
Phenopthalein(PP)	8-11	550	Colorless to pink
Bromothymol blue(BTB)	6-8	615	Yellow to blue

2.5 Standardization of Solutions:

Carbon dioxide solution was standardized using a standard sodium hydroxide solution. DEA solution was standardized using a standard hydrochloric acid solution. Both the titrations were conducted, just before the run.

2.6 Maintenance of pH:

The pH of the reacting solution was maintained using a digital pH meter (ELICO). The reagents used to adjust pH were sodium hydroxide and hydrochloric acid.

2.7 Calibration of Equipment:

The reliability of the equipment was checked using sodium hypochlorite – sodium sulfite system. The average of the second order rate constant was found to be 7800 $\pm$ 200 lit/gmole sec at 306 K. Concentration ranges of hypochlorite and sulfite were 0.004 – 0.006 M and 0.008 – 0.01 M, respectively. A pH of 11.0 and an ionic strength of 0.034 M were maintained. The value of the second order rate constant agreed with the accepted values [27, 28]. These authors used a flow thermal method to study this reaction.

2.8 Experimental Procedure:

To prepare aqueous solution of CO_2 before each run, pure CO_2 gas, was bubbled through a sparger, into double distilled water. A magnetic stirrer was used to ensure uniform concentration of carbon dioxide solution. DEA solutions was made by diluting the known amount of amine with double distilled water. Both the solutions were titrated to find out the concentrations of reactants before the run. Depending on the indicator used, wavelength given in Table 2, was set in the wavelength setter. When the two reactants were mixed, in the mixing cell, by pushing the driving syringes, an output signal of voltage as a function was noted in the oscilloscope.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Treatment of Data:

The experimental data for the runs have been presented
in Appendix. The output signal of voltage with respect to time
was recorded for each run. This voltage data were converted
to the absorbence of the reference reactant, using instrument
correlations, given in Appendix.

3.2 Effect of Concentration:

A number of runs were carried out at various DEA concen-
trations. The data have been presented in Tables A1, A2 and
A3 of Appendix. All the experiments were conducted at 298 K
and 9.5 pH. Concentration of amine was varied from 0.072-0.097M
and CO_2 concentration was maintained at 0.005M. Indicator
(phenophthalein) concentration was maintained at 2.5×10^{-5} M for
all the runs. A pseudo first order condition with excess
amine prevailed. Plots of logarthms of absorbance versus time
were made to test the pseudo first order condition for all the
runs. The slope of this plot gives k_{obs} value. A typical
plot of logarthm of absorbance, as a function of time for
0.097 M amine concentration and 0.0053 M CO_2 concentration
at 298 K and 9.5 pH, is shown in Figure 2, for run C1. As
shown in Figure 2, the experimental data were correlated by a
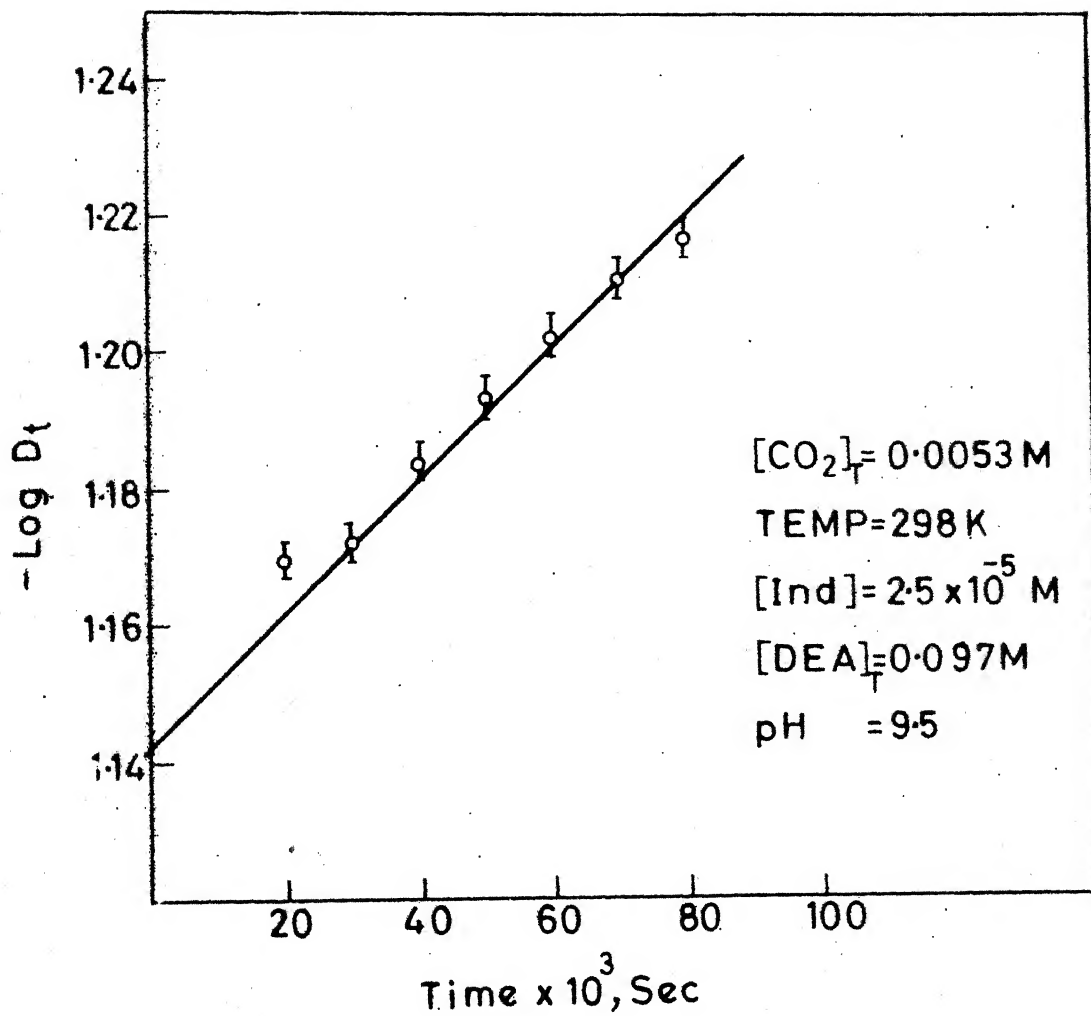
Fig. 2 Pseudo first order test for experimental data

straight line indicating the pseudo first order reaction.
Overall second order rate constants, k_2, were calculated by
dividing k_{obs}, with the amine concentrations. Calculated
values of the rate constants for the runs are shown in
Table 3.

TABLE 3 : CALCULATED VALUES OF RATE CONSTANTS
AT 9.5 pH AND 298 K

Run No.	DEA Conc., M	CO_2 Conc., M	k_{obs}, sec^{-1}	k_2, lit/gmole sec.
C-1	0.097	0.0053	2.45 ± 0.12	25 ± 1.3
C-2	0.084	0.0053	2.35 ± 0.13	28 ± 1.6
C-3	0.071	0.0053	1.79 ± 0.10	25 ± 1.5

From Table 3, it was observed that the overall second order
rate constant value, k_2 was 26 ± 1.6 **lit/g mole sec** at
298 K and 9.5pH.

3.3 Effect of Temperature:

A number of experiments were carried out at various
temperatures ranging from 293 K to 313 K. The data have been
presented in Tables A-4 to A-8 of Appendix. Concentrations
of DEA and CO_2 were maintained at 0.097 M and 0.0053 M,
respectively for all the runs and a pH of 9.5 was maintained.
Phenopthalein indicator, 2.5×10^{-5} M concentration was used
in all the runs. A pseudo first order condition was assumed

and the experimental data were correlated to a straight line, as done in Section 3.2. Calculated values of the rate constants for various runs were presented in Table 4 .

TABLE 4: CALCULATED VALUES OF RATE CONSTANTS AT 9.5 pH

Run No.	DEA Conc., M	CO_2 Conc., M	Temperature, K	k_{obs} sec^{-1}	k_2, lit/gmole sec.
C-4	0.097	0.0053	313	5.37 ± 0.3	55 ± 3.46
C-5	0.097	0.0053	308	3.52 ± 0.28	36 ± 2.97
C-6	0.097	0.0053	303	2.66 ± 0.17	27 ± 1.82
C-7	0.097	0.0053	298	2.45 ± 0.18	25 ± 1.92
C-8	0.097	0.0053	293	1.7 ± 0.24	18 ± 2.48

Figure 3 shows an Arrhenius plot of the values of the second order rate constant, k_2 against $1/T$. The apparent activation energy was found to be 46.3 KJ/gmole. The value of apparent activation energy is in close agreement with the reported values (Table 1).
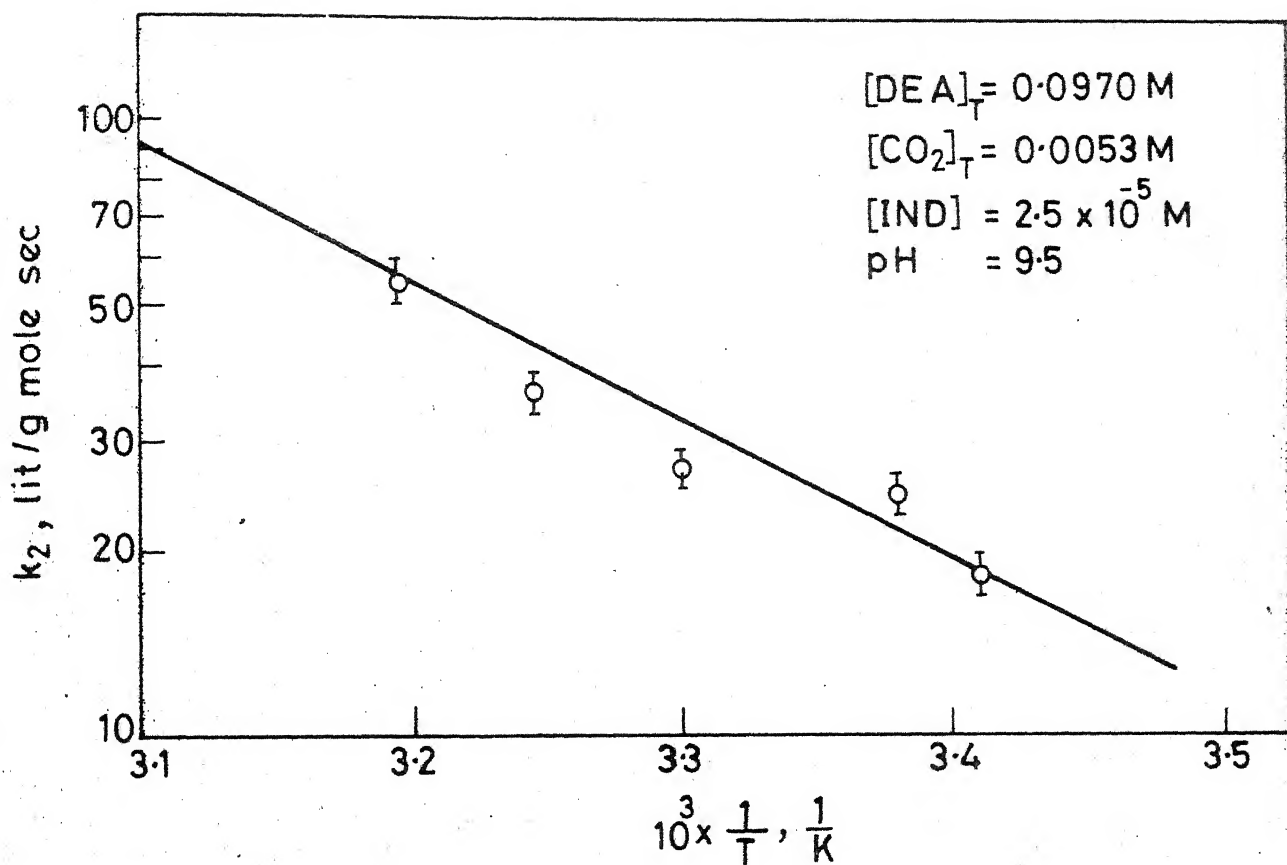
Fig. 3 Arrhenius plot for activation energy

3.4 Species Distribution of Reactants:

Species distribution for both CO_2 and DEA were computed as a functional of pH. The concentrations of all the reactive species present in the system were computed using the equilibrium constants [19] and the total concentrations of both CO_2 and DEA. The species present in CO_2 system are CO_3^{--}, CO_2 free, HCO_3^- and H_2CO_3 and the species present in DEA system are AmH^+ and $Am_{,free}$. The total concentrations of CO_2 and DEA are 5.36×10^{-3} M and 9.7×10^{-2} M, respectively. The species distribution for CO_2 system was calculated as follows:

$$[CO_2]_T = [CO_3^{--}] + [HCO_3^-] + [H_2CO_3] + [CO_2]_{free}$$

(12)

where $[CO_2]_T$ represents, the total concentration of CO_2 present in all its forms. The concentrations of HCO_3^-, H_2CO_3, and $CO_{2,free}$ were written in terms of CO_3^{--} concentration and respective equilibrium constants given in Table 5 [19]. Equation (12) then becomes

$$[CO_2]_T = [CO_3^{--}] \left(1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]^2}{K_1 K_2 K_h} \cdot\right)$$

(13)

At a particular hydrogen ion concentration, $[CO_3^{--}]$ was computed from equation (13). The concentrations of HCO_3^-, H_2CO_3 and $CO_{2,free}$ are calculated from CO_3^{--} concentration and their respective equilibrium constants (Table 5). The distribution of various species in the CO_2 system are shown in Figure 4, as percentages of the total CO_2 concentration, $[CO_2]_T$.
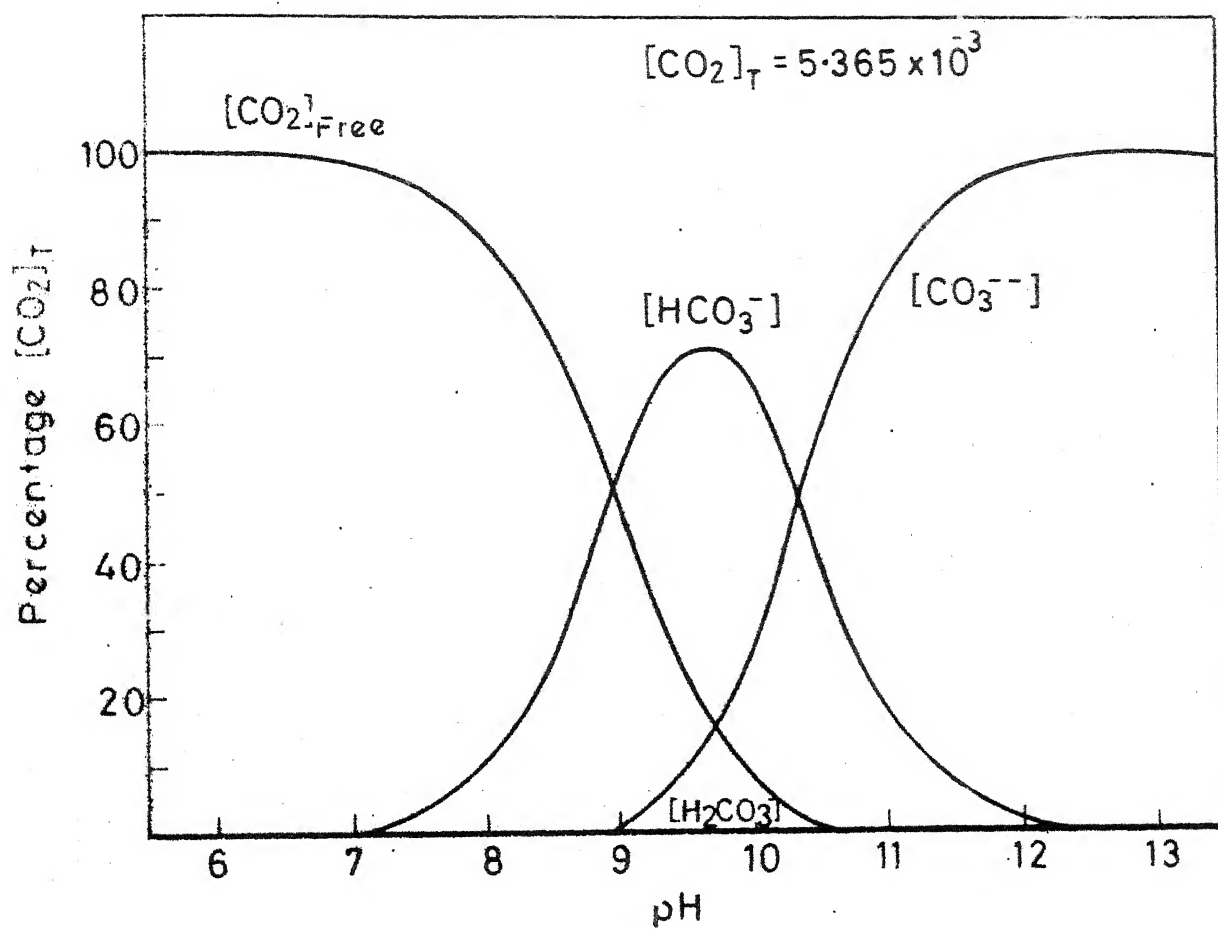
Fig.4 Species distribution of Carbon dioxide at $[CO_2]_T = 0.0053M$

Similarly distribution of species in the DEA system was computed using the protonation constant K_A of DEA (Table 5) and the equation given below:

$$[Am]_T = [Am]_{free} \left(1 + K_A [H^+] \right) \tag{14}$$

where $[Am]_T$ is the total diethanolamine concentration. The distribution of species is shown in Figure 5 as percentage of total amine concentration, $[Am]_T$.

TABLE 5: EQUILIBRIUM CONSTANTS AT 298 K TO CALCULATE SPECIES DISTRIBUTION OF CO_2 AND DEA [19]

Constant	Reaction System	Value at 298 K
K_h	$CO_2 + H_2O \rightleftharpoons H_2CO_3$ $K_h = (H_2CO_3)/(H_2O)(CO_2)$	2.59×10^{-3}
K_1	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $K_1 = (H^+)(HCO_3^-)/(H_2CO_3)$	$4.43 \times 10^{-7} M$
K_2	$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$ $K_2 = (H^+)(CO_3^{--})/(HCO_3^-)$	$4.57 \times 10^{-11} M$
K_A	$Am + H^+ \rightleftharpoons AmH^+$ $K_A = (AmH^+)/(Am)(H^+)$	$1 \times 10^{-8.83} M$

3.5 Effect of pH:

A number of runs were carried out at various pH values ranging from 7.50 to 11.25 in order to determine the effect of

Fig.5 Species distribution of DEA at $[Am]_T = 0.097M$

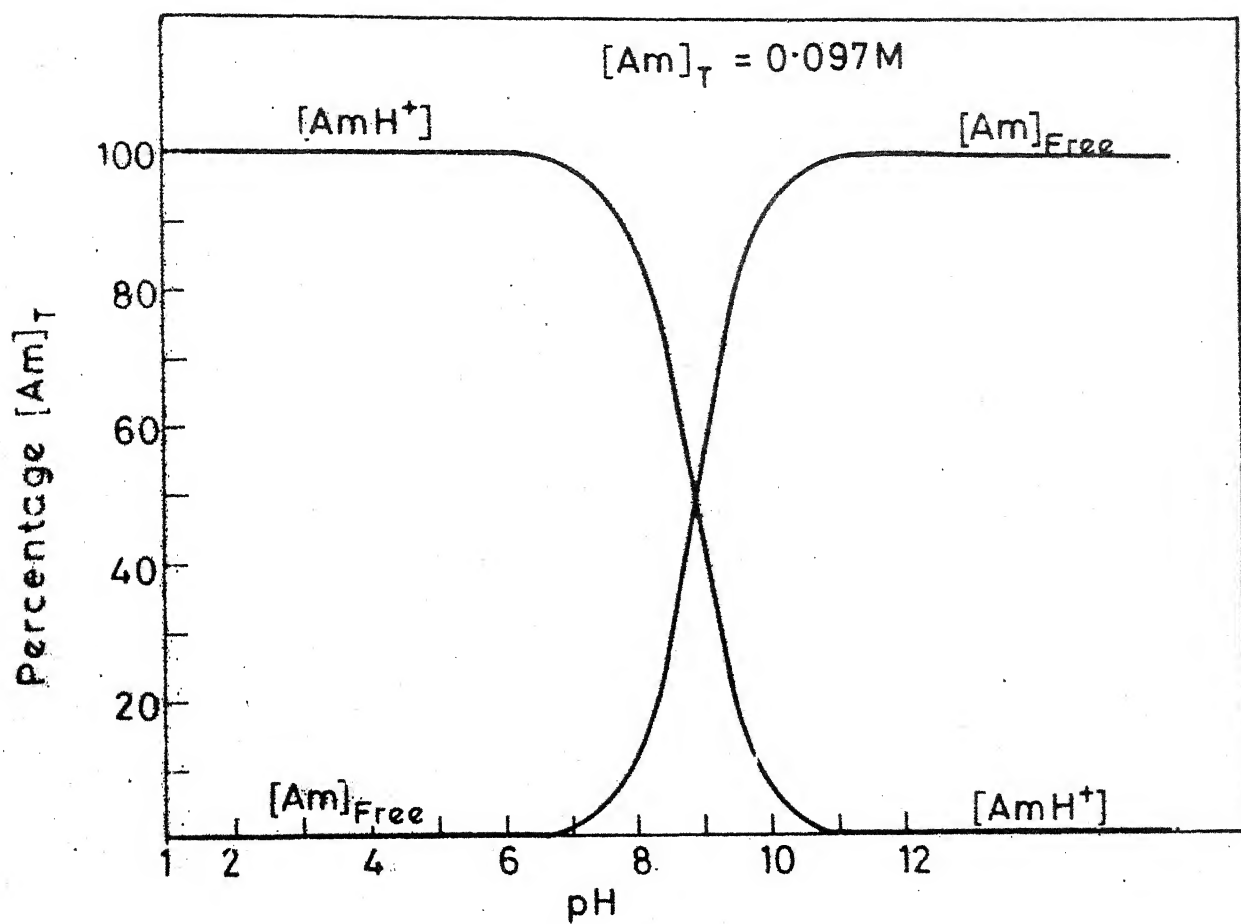hydrogen ion concentration on CO_2-DEA reaction. The data have been presented in Tables A-9 to A-17 of Appendix. All the runs were carried out at 9.7×10^{-2} M DEA, 5.36×10^{-3}M CO_2 and 2.5×10^{-5} indicator concentrations and at 298 K. Pseudo first order rate constants were calculated from the slopes of log D_t versus time curves which were linear. The procedure has been described in Section 3.2. Calculated values of rate constants at various pH values are given in Table 6. The pH profile of rate constant values is shown in Figure 6. From Figure 6 and Table 6, it was observed that the rate constant, k_2, increases linearly upto a pH value of 10.5 and levels off at pH $>$ 11.

TABLE 6: CALCULATED VALUES OF RATE CONSTANTS AT VARIOUS pH VALUES AND AT [DEA] = 0.097M, [CO_2] = 0.0053M, [Ind] = 2.5×10^{-5} M and T = 298 K

Run No.	pH	k_{obs}, Sec.$^{-1}$	k_2, lit/mole sec.
C-9	7.50	1.67 ± 0.10	17.2 ± 0.92
C-10	7.75	1.85 ± 0.06	19.1 ± 0.64
C-11	8.00	1.94 ± 0.08	20.0 ± 0.78
C-12	8.50	2.38 ± 0.23	24.6 ± 2.32
C-13	9.00	2.75 ± 0.32	28.4 ± 3.28
C-14	10.00	3.68 ± 0.45	38.0 ± 4.62
C-15	10.50	3.85 ± 0.34	39.8 ± 3.54
C-16	11.00	4.11 ± 0.35	42.4 ± 3.60
C-17	11.25	4.15 ± 0.36	42.8 ± 3.76
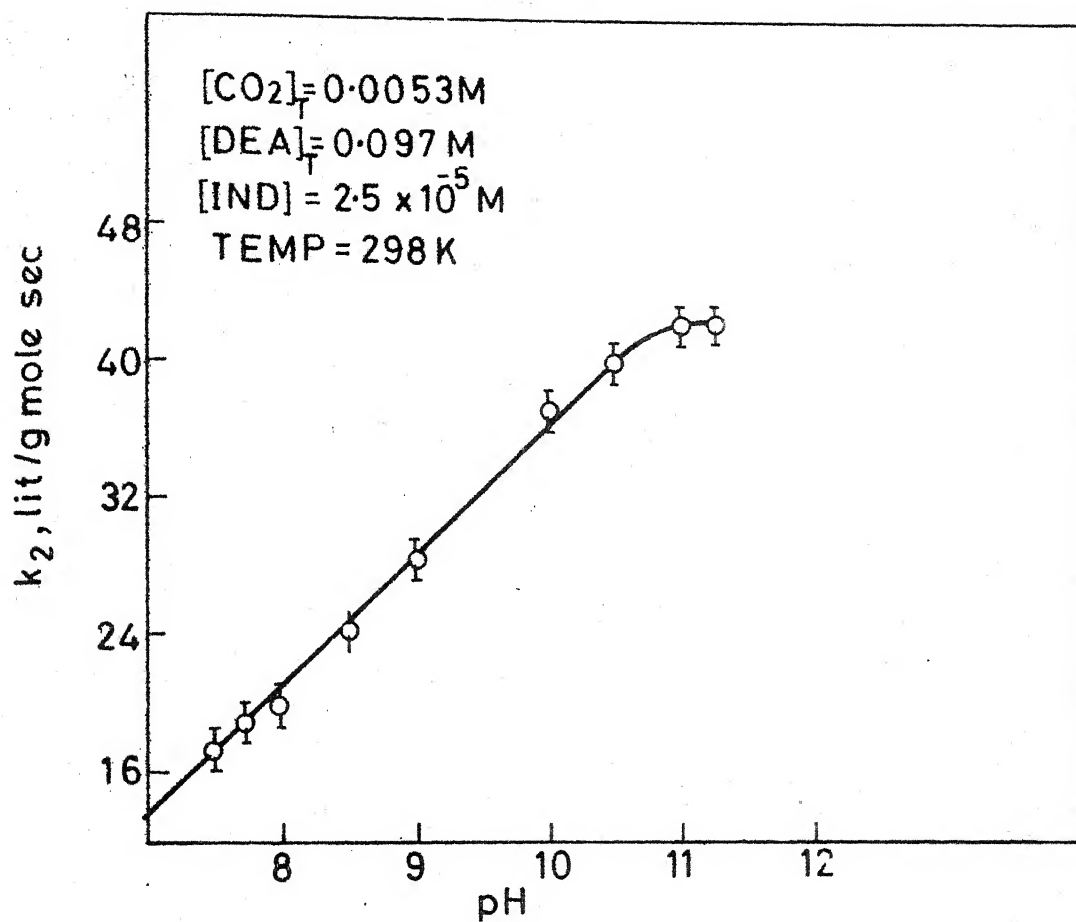
Fig.6 Calculated values of rate constant as function of pH

The species distributions given in Figures 4 and 5 were used to identify the predominant reactive species present at a particular value of pH. Assuming the presence of protonated and unprotonated forms of DEA on one hand and $CO_{2,free}$, HCO_3^-, CO_3^{--} on the other, the following rate equation has been postulated,

$$\text{Rate} = k_2 [Am]_T [CO_2]_T \tag{15}$$

where Am represents diethanolamine. In the pH range 7.5-8.0, the species present in the reaction system are $CO_{2,free}$, $Am\ H^+$ and Am_{free} (Figures 4 and 5). Equation (15) can be written as

$$\text{rate} = k_2 [Am]_T [CO_2]_T = k_{Am\ H^+}^{CO_{2,free}} [Am\ H^+][CO_2]_{free}$$

$$+ k_{Am,free}^{CO_{2,free}} [Am]_{free} [CO_2]_{free}$$

$$= k_{Am\ H^+}^{CO_{2,free}} K_A [Am]_{free} [H^+][CO_2]_{free}$$

$$+ k_{Am,free}^{CO_{2,free}} [Am]_{free} [CO_2]_{free} \tag{16}$$

or

$$k_2 \frac{[Am]_T}{[Am]_{free}} \frac{[CO_2]_T}{[CO_2]_{free}} = k_{Am,free}^{CO_{2,free}} + k_{Am\ H^+}^{CO_{2,free}} K_A [H^+] \tag{17}$$

where

$$\frac{[Am]_T}{[Am]_{free}} = 1 + K_A [H^+] \quad \text{and} \quad \frac{[CO_2]_T}{[CO_2]_{free}} = 1 \text{ in the pH range of}$$

7.5 - 8.0.

A plot of left hand side of Equation (17) versus $[H^+]$ gives a straight line, as shown in Figure 7, with an intercept $k_{Am,free}^{CO_2,free} = 13.77 \pm 2$ lit/gmole sec and a slope $k_{AmH^+}^{CO_2,free} K_A = 1.27 \times 10^{10}$ or $k_{AmH^+}^{CO_2,free} = 18.89 \pm 2$ lit/gmole sec.

In the pH range 8.0 -9.0, the species present are AmH^+ and $Am_{,free}$ on one hand and $CO_{2,free}$ and HCO_3^- on the other (Figures 4 and 5). A rate expression suitable for this pH range is formulated below:

$$\text{rate} = k_2[Am]_T [CO_2]_T = k_{AmH^+}^{CO_2,free}[AmH^+][CO_2]_{free} + k_{AmH^+}^{HCO_3^-} [AmH^+] [HCO_3^-]$$

$$+ k_{Am,free}^{CO_2,free} [Am]_{free} [CO_2]_{free} + k_{Am,free}^{HCO_3^-}[Am]_{free} [HCO_3^-] \quad (18)$$

rearrangement of terms gives

$$\frac{k_2 [Am]_T [CO_2]_T}{[Am]_{free}[CO_2]_{free}} - k_{AmH^+}^{CO_2,free} K_A [H^+] - k_{Am,free}^{CO_2,free}$$

$$= k_{AmH^+}^{HCO_3^-} K_A K_1 K_h + \frac{k_{Am,free}^{HCO_3^-} K_1 K_h}{[H^+]} \quad (19)$$

where

$$\frac{[Am]_T}{[Am]_{free}} = 1 + K_A [H^+] \quad \text{and} \quad \frac{[CO_2]_T}{[CO_2]_{free}} = 1 + \frac{K_1 K_h}{[H^+]}.$$

A plot of left hand side of Equation (19) versus $1/[H^+]$ (Figure 8)
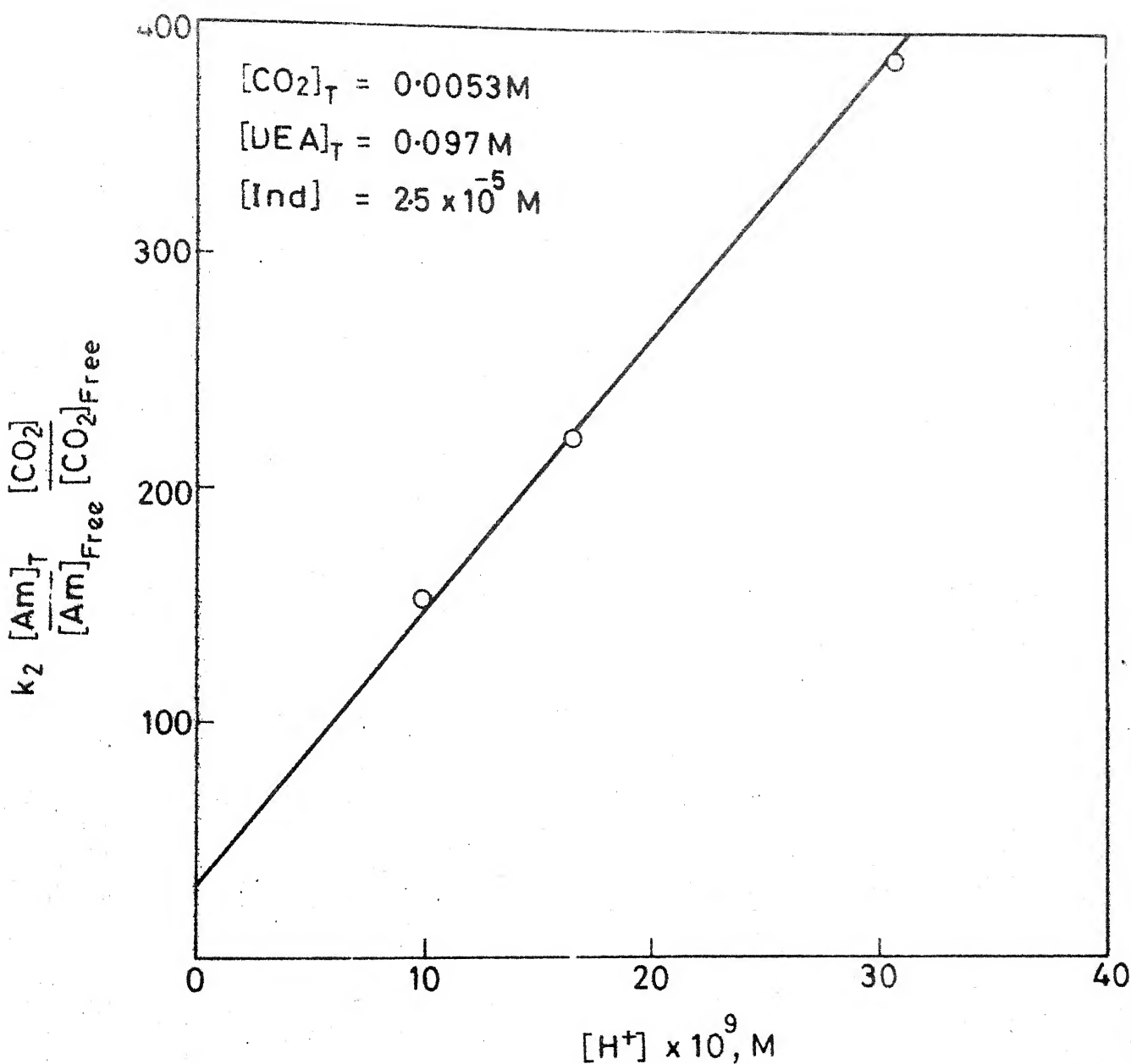
Fig.7 Resolution of the rate constants $k_{Am_{free}}^{CO_{2free}}$ and $k_{AmH^+}^{CO_{2free}}$ at 298K

The figure shows a plot with y-axis labeled $k_2 \dfrac{[Am]_T}{[Am]_{Free}} \dfrac{[CO_2]}{[CO_2]_{Free}}$ and x-axis labeled $[H^+] \times 10^9, M$.

$[CO_2]_T = 0.0053 M$

$[DEA]_T = 0.097 M$

$[Ind] = 2.5 \times 10^{-5} M$
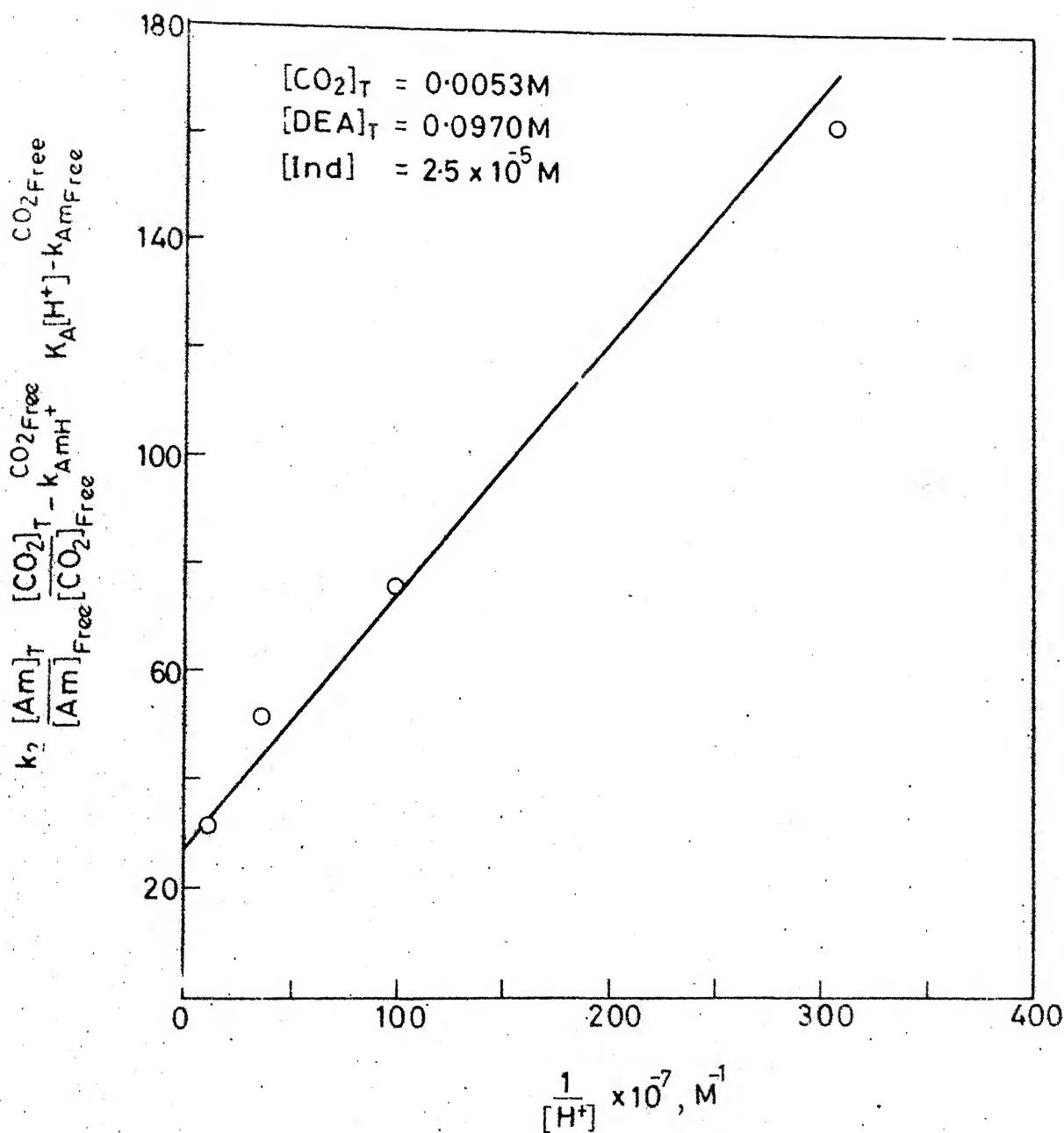
Fig.8 Resolution of the rate constants $k_{Am_{free}}^{HCO_3^-}$ and $k_{AmH^+}^{HCO_3^-}$ at 298 K

gives $k_{AmH^+}^{H \cdot CO_3^-} = 34.80 \pm 4$ lit/gmole sec and $k_{Am,free}^{HCO_3^-} = 0.025 \pm 0.005$ lit/gmole sec. The values for $k_{Am,free}^{CO_2,free}$ and $k_{AmH^+}^{CO_2,free}$ were inserted from earlier deduction.

Finally in the pH range 9.0–10.5, species present are $CO_2,free$, HCO_3^- and CO_3^{--} on one hand and AmH^+ and Am_{free} on the other. An expression suitable for this pH range is written as below:

$$\text{rate} = k_2 [Am]_T [CO_2]_T = k_{Am,free}^{CO_2,free} [Am]_{free} [CO_2]_{free}$$

$$+ k_{AmH^+}^{CO_2,free} [AmH^+][CO_2]_{free} + k_{Am,free}^{HCO_3^-} [Am]_{free}[HCO_3^-]$$

$$+ k_{AmH^+}^{HCO_3^-} [AmH^+][HCO_3^-] + k_{Am,free}^{CO_3^{--}} [Am]_{free} [CO_3^{--}]$$

$$+ k_{AmH^+}^{CO_3^{--}} [AmH^+] [CO_3^{--}] \qquad (20)$$

Algebric manipulation similar to the ones derived above gives the following expression

$$\left\{ k_2 [H^+] \frac{[CO_2]_T}{[CO_2]_{free}} \frac{[Am]_T}{[Am]_{free}} \right\} - \left\{ k_{AmH^+}^{CO_2,free} K_A [H^+]^2 + k_{Am,free}^{CO_2,free} [H^+] \right.$$

$$\left. + k_{Am,free}^{HCO_3^-} K_1 K_h + k_{AmH^+}^{HCO_3^-} K_A K_1 K_h [H^+] \right\}$$

$$= k_{AmH^+}^{CO_3^{--}} K_A K_1 K_2 K_h + k_{Am,free}^{CO_3^{--}} \frac{K_1 K_2 K_h}{[H^+]} \qquad (21)$$

where $\dfrac{[Am]_T}{[Am]_{free}} = 1 + K_A [H^+]$ and $\dfrac{[CO_2]_T}{[CO_2]_{free}} = 1 + \dfrac{K_1 K_h}{[H^+]} + \dfrac{K_1 K_2 K_h}{[H^+]^2}$.

A plot of left hand side of Equation (21) versus $1/[H^+]$ (Figure 9) gives $k_{AmH^+}^{CO_3^{--}} = 265.07 \pm 9$ lit/gmole sec and $k^{CO_3^{--}} = 51.54 \pm 4$ lit/gmole sec. Values for $k_{Am,free}^{CO_2,free}$, $k_{AmH^+}^{CO_2,free}$, $k_{Am,free}^{HCO_3^-}$ and $k_{AmH^+}^{HCO_3^-}$ were inserted from the previous deductions. The values of individual rate constants thus determined are presented in Table 7. It is observed at pH $>$ 11, the only important reaction taking place is between CO_3^{--} and Am,free (Figures 4 and 5), and this rate constant (51.5 ± 4 lit/gmole sec) is in agreement with the rate constant observed at pH 11 (43 ± 4 lit/gmole sec., Figures 6 and Table 6).

TABLE 7: CALCULATED VALUES OF INDIVIDUAL RATE CONSTANTS OF DIFFERENT REACTIONS AT 298 K

Individual rate constant	Value, in lit/gmole sec.	Individual rate constant	Value, in lit/gmole sec.
$k_{Am,free}^{CO_2,free}$	13.77 ± 2	$k_{AmH^+}^{HCO_3^-}$	34.80 ± 4
$k_{Am,H^+}^{CO_2,free}$	18.89 ± 2	$k_{Am,free}^{CO_3^{--}}$	51.54 ± 4
$k_{Am,free}^{HCO_3^-}$	0.0249 ± 0.005	$k_{AmH^+}^{CO_3^{--}}$	265.07 ± 9

Table 7 shows that the value of $k_{Am,free}^{HCO_3^-}$ is negligible compared to other rate constants implying that the forward rate of Equation (22) is much too small compared to the
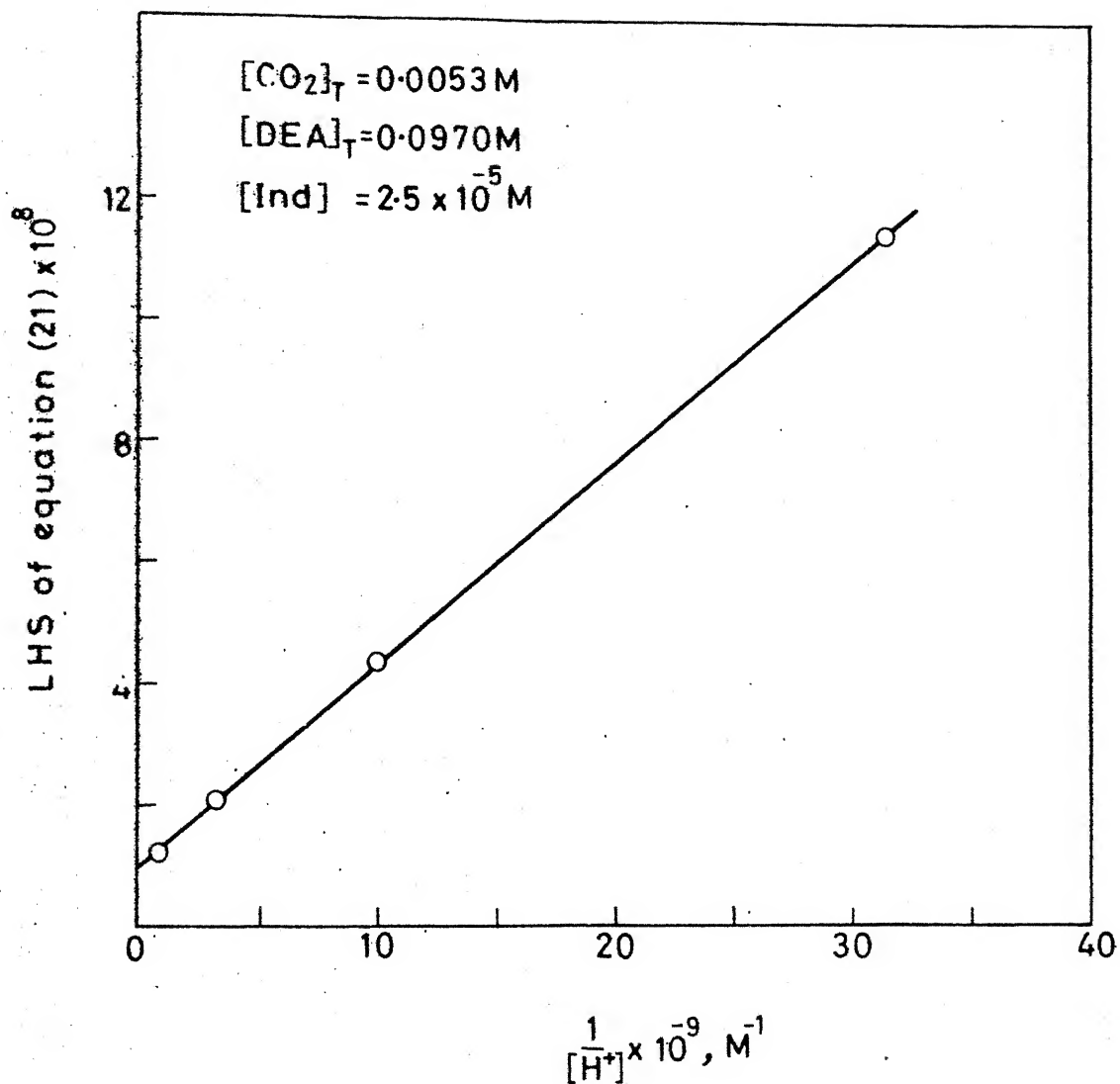
Fig. 9 Resolution of the rate constants $k_{Am_{free}}^{CO_3^{--}}$ and $k_{AmH^+}^{CO_3^{--}}$ at 296K

$$Am + HCO_3^- \rightleftharpoons Products \qquad (22)$$
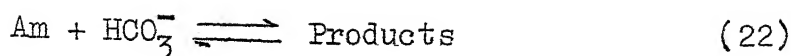
reverse reaction and other reactions taking place in the DEA-CO_2 system.

A mechanism consistent with these experimental results is proposed as under

$$R_2NH + CO_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_2\overset{+}{N}H\ CO_2^- \qquad (rds) \qquad (23)$$

$$R_2\overset{+}{N}HCO_2^- + R_2NH \xrightarrow{k_3} R_2NCO_2^- + R_2NH_2^+ \cdot$$

$$\qquad\qquad (fast) \qquad (24)$$
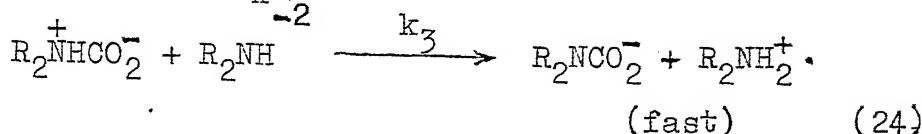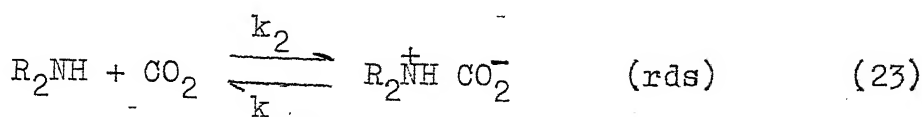
The steady state approximation on the intermediate $R_2\overset{+}{N}H\ CO_2^-$ gives the rate of disappearance of carbon dioxides as

$$-\frac{d\ [CO_2]}{dt} = \frac{k_2 k_3\ [Am]^2\ [CO_2]}{k_{-2} + k_3\ [Am]} \cdot \qquad (25)$$

The ratio $[Am]/[CO_2]$ is approximately 20 in these experiments and is much higher in actual industrial absorption systems, so the reverse rate constant k_{-2} is very small [18]. Proton transfer step (24) is believed to be very fast as in many reactions involving proton transfer. For the above cases, $k_{-2} \ll k_3\ [Am]$ and the Equation (25) reduces to

$$-\frac{d\ [CO_2]}{dt} = k_2\ [Am][CO_2] \cdot \qquad (26)$$

Thus forward reaction of Equation (23) becomes the rate limiting step of the process and Equation (26) represents an overall second order reaction, (i.e.), first order in amine as well as in carbon dioxide. The experimental results obtained in this

investigation are in agreement with these assumptions.

The mechanism proposed herein does not agree with some of the earlier literature reports [5,9,16]. Hikita et al [9] investigated this reaction, with DEA concentration range of 0.174 M - 2 M and reported an overall third order kinetics, (i.e.) second order with respect to amine and first order with respect to CO_2. They argued that the proton transfer step (24) becomes rate limiting because of the steric requirements in DEA. But it is hard to believe that, a proton transfer step can be so slow that it becomes rate controlling, whatever the steric requirement may be. The overall reaction order from the present study is shown to be two, which is in agreement with most of the literature data[3,21,12,24,10,7,8,18]. However, the reaction rate constant k_2 (26±1.6 lit/gmole sec at 298 K) obtained in the present study is small compared with the values reported in the literature. This may be due to the fact that most of the experiments were conducted at sufficiently high concentrations of reactants, while experiments of this study were conducted at very low concentrations. Most of the reaction rate constants (k_2) of previous authors were measured indirectly by using gas absorption techniques. The indirect methods involve the hydration of CO_2, when CO_2 is absorbed in aqueous solution of DEA. The contribution from hydration of CO_2 may be one of the important reasons for the high values of rate constants reported by earlier authors[3,7,21].

The procedure adopted for resolving the rate constants due to different chemical species present in the system has been explained before. The possible reactions are listed below:

Rate Constants

$$R_2NH + CO_2 \xrightarrow{13.77} R_2N^+HCOO^- \tag{27}$$

$$R_2NH + HCO_3^- \xrightarrow{0.025} R_2NCOO^- + H_2O \tag{28}$$

$$R_2NH + CO_3^{--} \xrightarrow{51.5} R_2NCOO^- + OH^- \tag{29}$$

$$R_2NH_2^+ + CO_2 \xrightarrow{18.89} R_2\overset{+}{NH}COO^- + H^+ \tag{30}$$

$$R_2NH_2^+ + HCO_3^- \xrightarrow{34.8} R_2\overset{+}{NH}COO^- + H_2O \tag{31}$$

$$R_2NH_2^+ + CO_3^{--} \xrightarrow{265} R_2NCOO^- + H_2O . \tag{32}$$
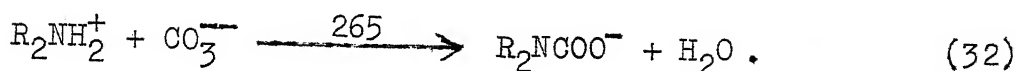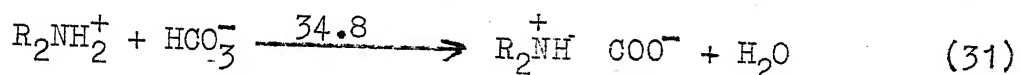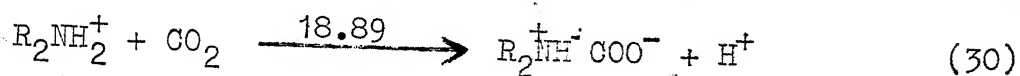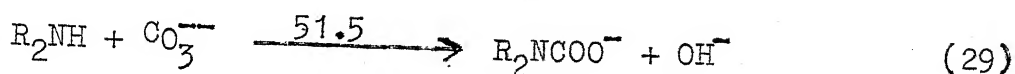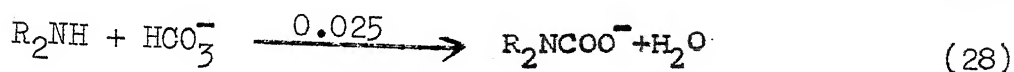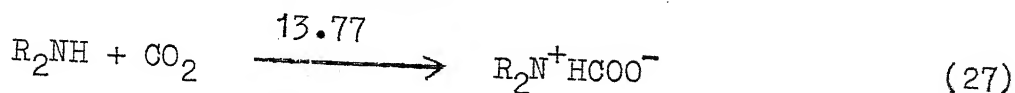
All these reactions contribute towards **the observed second** order rate constants calculated at different pH values as given in Table 6 and Figure 6.

The reaction can be visualised according to a scheme given below. Three examples have been choosen as illustrations

(Reaction of Eq.27)

$$\tag{33}$$

(Reaction of Eq.29)

$$\tag{34}$$

(Reaction of Eq.31)

$$\underset{R}{\overset{R}{>}}\overset{\overset{H}{\underset{\oplus}{N}}}{N} - H + \left[\begin{array}{c} O-H \\ C \\ O \quad O \end{array}\right]^{-} \xrightarrow{34.8} \underset{R}{\overset{R}{>}}N-C\overset{O^{-}}{\underset{O}{}} + H_2O.$$

$$(35)$$
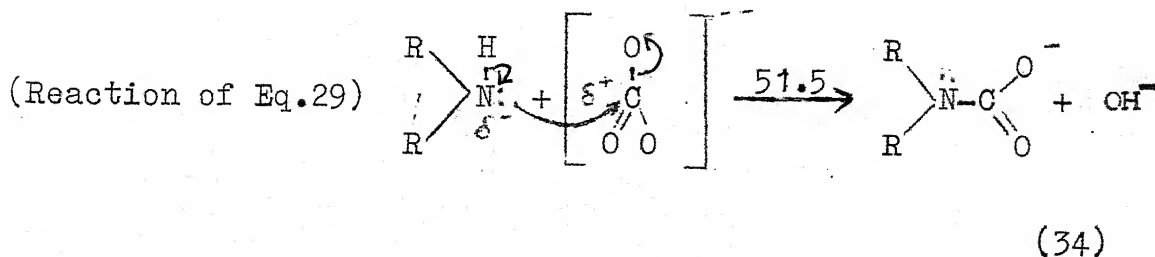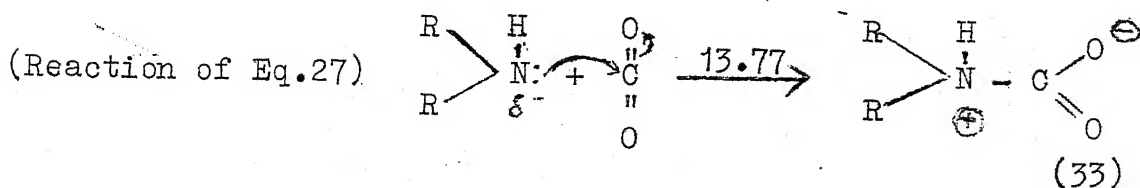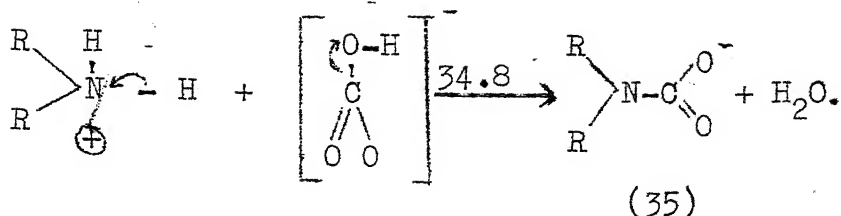
A look at the rate constants will reveal the effect of charge on the rate. The rate constants involving charged species are higher than the uncharged species. With the same species $R_2NH_2^+$, the rate increases in the order $CO_2 < HCO_3^- < CO_3^{--}$. Similarly for R_2NH species, the rate constants follow the same order with an exception of HCO_3^- (reaction of Eq.(28)). It appears that the carbamate formation does not take place to any appreciable extent by reaction of Eq.(28). And the reaction that can be considered from HCO_3^- and R_2NH is

$$R_2NH + HCO_3^- \longrightarrow R_2NH_2^{++} + CO_3^{--}. \qquad (36)$$
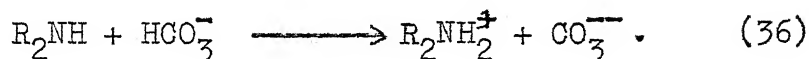
This reaction was considered by Savage and Kim [29], who considered that the reaction would not be significant because of the differences in pK values of $R_2NH = 8.8$ at 298 K and $HCO_3^- = 10.4$ at 298 K.

It is also pointed out that the value of k_2 in the present study at pH = 10 and at 298 K, is 38 ± 4 lit/gmole sec as compared to 110 ± 15 deduced by Barth et al.[18], from their studies in which DEA = $(0.111 - 8.4) \times 10^{-2}$M and $CO_2 = (2.94-5.6) \times 10^{-3}$M and temperature = 298 K. The activation energy in this study was calculated as 46.3 KJ/mole, which is in agreement with the values reported in literature (Table 1).

CHAPTER 4

CONCLUSIONS

The homogeneous kinetics of reaction of carbon dioxide and diethanolamine was studied using stopped flow apparatus. The experimental results showed that the reaction is second order, (i.e.) first order with respect to both carbon dioxide and diethanolamine., The pseudo first order fit prevailed and the value of overall second order rate constant was calculated as 26 ± 1.6 lit/gmole sec at 298 K and at a pH of 9.5. The value of apparent activation energy was calculated as 46.3 KJ/mole.

The pH dependence of reaction rate constants was used for resolving the individual rate constants for pairs of reactive species present in the system. A mechanism consistent with the experimental results was proposed as follows:

$$R_2NH + CO_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} R_2\overset{+}{N}HCO_2^- \qquad (r\ d\ s) \quad (23)$$

$$R_2\overset{+}{N}HCO_2^- + R_2NH \overset{k_3}{\longrightarrow} R_2NCO_2^- + R_2NH_2^+ \ (fast). \ (24)$$
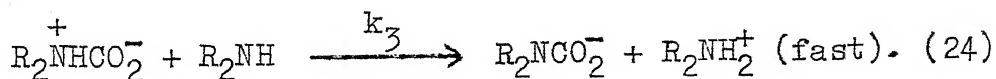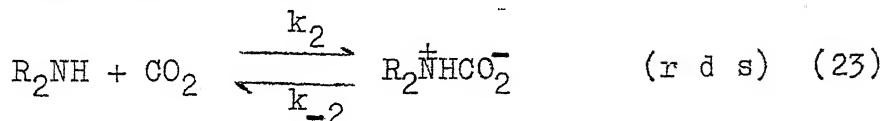
It was found that the reaction step (23) was rate determining step in which k_{-2} was negligible compared with k_3. The experimental data were satisfactorily correlated with the rate expression

$$-\frac{d\,[CO_2]}{dt} = k_2\,[Am]\,[CO_2].\tag{26}$$

This is the first report on resolution of individual rate constants for this reaction. It was also pointed out that there is one of the few investigations made on this reaction by direct chemical means.

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<u>A P P E N D I X</u>

INSTRUMENT CORRELATIONS

The following correlations were used to convert the raw data (i.e., voltage data) in terms of absorption versus time.

$$V_t = V_{io} - (G_t \times Z) \qquad\qquad A1$$

$$D_t = 1.6 \; Log_{10} \frac{V_o}{V_t} \qquad\qquad A2$$

where V_t is transmitted light intensity with sample at time t; V_o is the transmitted light intensity with a non absorbing sample; G_t is the number of voltage graduations at time t; Z is the amount of intensity of one graduation of the output signals and D_t, is the optical density.

Experimental data were presented in the following Tables.

TABLE A-1: EXPERIMENTAL DATA AT 298 K and 9.5 pH

V_o = 2.5V, V_{io} = 2.3V,   Z = 0.002, [DEA] = 0.097 M and
[CO_2] = 0.0053 M   [Ind] = 2.5 x 10^{-5}M, Run C-1

Time, (mill sec)	Graduations	Log D_t
20	16	-1.1695
30	15.5	-1.1715
40	12.5	-1.1835
50	10	-1.1937
60	8	-1.2021
70	6	-1.2108
80	5	-1.2149
90	4	-1.2192

TABLE A-2: EXPERIMENTAL DATA AT 298 K AND 9.5 pH

$V_o = m2.5V$, $V_{io} = 2.45V$, $[DEA] = 0.084$ M and $[CO_2] = 0.0053M$ $Z = 0.001$, $[Ind] = 2.5 \times 10^{-5}M$

Run C-2

Time (Milli sec)	Graduations	Log D_t
2	13	-1.7511
5	12.5	-1.7546
10	11	-1.7657
15	10	-1.7726
20	9	-1.7800
25	8	-1.7875
30	7.5	-1.7913
35	7	-1.7951
40	6.5	-1.7990
45	6	-1.8029
50	5.5	-1.8068

TABLE A-3: EXPERIMENTAL DATA AT 298 K, 9.5 pH
AND DEA = 0.071 M

$[CO_2]$ = 0.0053M, V_o = 2.5V, V_{io} = 2.3V

and Z = 0.002 [Ind] = 2.5×10^{-5} M,

Run C-3

Time (Milli sec.)	Graduations	Log D_t
10	10	-1.1937
20	8.5	-1.2021
30	7	-1.2106
40	6	-1.2171
50	5	-1.2236
60	4	-1.2258
70	3	-1.2292

TABLE A-4: EXPERIMENTAL DATA AT 313 K AND 9.5 pH

Temp. = 313 K, $[DEA]$ = 0.097 M , $[CO_2]$ = 0.0053 M

$[Ind]$ = 2.5x10^{-5}M, V_0 = 2.5V, V_{io} = 2.3V,

Z = 0.002   Run C-4

Time (milli sec.)	Graduations	log D_t
10	41	-1.0800
15	40	-1.0833
20	39	-1.0866
25	34.5	-1.1018
30	31	-1.1139
35	27	-1.1282
40	23.5	-1.1409
45	20	-1.1540
50	17.5	-1.1637
55	15.5	-1.1715
60	14	-1.1775
65	12.5	-1.1835
70	10.5	-1.1917
75	9.5	-1.1958

TABLE A-5: EXPERIMENTAL DATA AT 308 K AND 9.5 pH

Temp. = 308 K,   [DEA] = 0.097 M, $[CO_2]$ = 0.0053 M

[Imd] = 2.5x10^{-5}M, $\bar{V}_o$ = 2.5V, V_{io} = 2.3V,   Z = 0.002

Run C-5

Time (Milli sec.)	Graduations	Log D_t
10	24	-1.1390
20	22	-1.1465
30	18.5	-1.1598
40	14	-1.1775
50	10	-1.1937
60	7	-1.2063
70	5	-1.2149
80	4	-1.2192
90	2.5	-1.2258

TABLE A-6: EXPERIMENTAL DATA AT 303 K AND 9.5 pH

Temp. = 303 K,   [DEA] = 0.097 M , [CO_2] = 0.0053 M

[Ind] = 2.5×10^{-5} M, V_0 = 2.5V, V_{io} = 2.3V,   Z=0.002

Run C-6

Time (Milli. sec)	Graduations	Log D_t
20	25	-1.1354
30	23	-1.1428
40	20.5	-1.1522
50	17	-1.1657
60	13.5	-1.1790
70	12	-1.1855
80	9.5	-1.1958
90	7.5	-1.2042

TABLE A-7: EXPERIMENTAL DATA AT 298 K AND 9.5 pH

Temp. = 298 K, [DEA] = 0.097M, [CO$_2$] = 0.0053 M

[Ind] = 2.5x10^{-5}M, V$_0$=2.5V, V$_{io}$=2.3V, Z = 0.002

Run C-7

Time (Milli sec)	Graduations	Log D$_t$
20	16	-1.1695
30	15.5	-1.1715
40	12.5	-1.1835
50	10	-1.1937
60	8	-1.2021
70	6	-1.2108
80	5	-1.2149
90	4	-1.2192

TABLE A-8: EXPERIMENTAL DATA AT 293 K AND 9.5 pH

Temp. = 293 K., $[DEA] = 0.097$ M, $[CO_2] = 0.0053$M

$[Ind] = 2.5 \times 10^{-5}$M, $V_o = 2.5$V, $V_{io} = 2.30$V, Z=0.002

Run C-8

Time (Milli sec.)	Graduations	Log D_t
10	10.5	-1.1896
20	8.5	-1.2021
30	7	-1.2106
40	6	-1.2171
50	5	-1.2236
60	4	-1.2258
70	3.5	-1.2298

TABLE A-9: EXPERIMENTAL DATA AT 298 K AND 7.5 pH

$$[DEA] = 0.097 \text{ M}, \quad [CO_2] = 0.005365 \text{ M},$$

$$[Ind] = 2.5 \times 10^{-5} \text{M} \quad V_o = 2.5 \text{ V} \quad V_{io} = 2.3 \text{ V}$$

$$Z = 0.001 \qquad \text{Run C-9}$$

Time (Milli sec.)	Graduations	Log D_t
2	13	-1.2084
5	12	-1.2106
8	10.5	-1.2138
10	9.5	-1.2159
15	8	-1.2192
20	6	-1.2286
25	5	-1.2258
30	4.5	-1.2269
35	4	-1.2280
40	3	-1.2302

TABLE A-10: EXPERIMENTAL DATA AT 298 K AND 7.75 pH

$[CO_2]$ = 0.005365 M, $[DEA]$ = 0.097 M, $[Ind]$ = 2.5x10^{-5}M

V_o = 2.5V, V_{io} = 2.3V,   Z = 0.001

Run C-10

Time (Milli sec.)	Graduations	Log D_t
2	18	-1.1979
5	16	-1.2022
10	13	-1.2080
15	11.0	-1.2127
20	9	-1.2170
25	8	-1.2192
30	7.0	-1.2214
35	6	-1.2236
40	5.5	-1.2247
45	4.5	-1.2269

TABLE A–11: EXPERIMENTAL DATA AT 298 K AND 8 pH

$[DEA] = 0.097$ M, $[CO_2]= 0.00536$ M,

$[Ind] = 2.5 \times 10^{-5}$ M $V_o = 2.5$ V, $V_{io} = 2.45$ V,

$Z = 0.001$

Run C–11

Time (Milli sec.)	Graduation	Log D_t
5	8.0	–1.7875
8	7.5	–1.7913
10	7.0	–1.7951
15	6.5	–1.7990
20	6.0	–1.8029
25	5.5	–1.8068
30	5.0	–1.8108
35	4.5	–1.8148
40	4.0	–1.8189
45	3.5	–1.8229
50	3.0	–1.8271
55	2.5	–1.8312

TABLE A-12: EXPERIMENTAL DATA AT 298 K AND 8.5 pH

$[DEA] = 0.097$ M, $[CO_2] = 0.005365$ M, $[Ind] = 2.5 \times 10^{-5}$ M

$V_o = 2.5$ V, $V_{io} = 2.45$ V $Z = 0.001$

Run C-12

Time (Milli sec)	Graduations	Log D_t
2	12	-1.7582
5	11.5	-1.7617
10	11.0	-1.7653
15	10.5	-1.7689
20	9.5	-1.7863
25	8.5	-1.7837
30	8	-1.7875
35	7.5	-1.7913
40	6.5	-1.7990
45	6	-1.8029
50	5.5	-1.8068
55	5	-1.8109

TABLE A–13: EXPERIMENTAL DATA AT 298 K AND 9 pH

$[\overline{DEA}] = 0.097$ M, $[\overline{CO_2}] = 0.005365$ M,

$[\overline{Ind}] = 2.5\text{x}10^{-5}$ M , $V_o = 2.5$V, $V_{io} = 2.40$V,

    $Z = 0.001$

Run C–13

Time (Milli sec.)	Graduations	Log D_t
2	16.5	−1.4793
5	15	−1.4852
7	14	−1.4890
10	13	−1.4929
15	11	−1.5008
20	9.5	−1.5069
25	7.5	−1.5151
30	6	−1.5213
35	4.5	−1.5277
40	4	−1.5298
45	3.5	−1.5319
50	3	−1.5340

TABLE A–14: EXPERIMENTAL DATA AT 298 K AND 10 pH

$[DEA] = 0.097M,$ $[CO_2] = 0.005365M,$ $[Ind] = 2.5 \times 10^{-5}M$

$V_{io} = 2.3V,$ $V_o = 2.5V,$ $Z = 0.001$

Run C–14

Time (Milli sec.)	Graduations	Log D_t
1		
20	50	−1.1354
25	47	−1.1409
30	45.5	−1.1437
35	39	−1.1560
40	33	−1.1676
45	27.5	−1.1785
50	22.5	−1.1886
55	18	−1.1979
60	15	−1.2042
65	13	−1.2084
70	12	−1.2106
75	11	−1.2127
80	10	−1.2149

TABLE A-15: EXPERIMENTAL DATA AT 298 K AND 10.5 pH

[DEA] = 0.097M,   [CO$_2$] = 0.005365M

[Ind] = 2.5x10^{-5}M V_o = 2.5V, V_{io} = 2.3V,

Run C-15

Time (Milli sec.)	Graduations	Log D_t
10	24	-1.1390
20	22	-1.1465
30	18.5	-1.1598
40	14	-1.1775
50	10	-1.1937
55	8	-1.2029
60	7	-1.2063
70	5	-1.2192

TABLE A-16: EXPERIMENTAL DATA AT 298 K AND 11.0 pH

$[\text{DEA}] = 0.097$ M, $[CO_2] = 0.0053$ M,

$[\text{Ind}] = 2.5 \times 10^{-5}$ M, $V_o = 2.5$V,

$V_{io} = 2.4$V, $Z = 0.001$

Run C-16

Time (Milli sec.)	Graduations	Log D_t
5	20	−1.466
10	18	−1.473
15	15	−1.485
20	13	−1.492
25	11.5	−1.498
30	10	−1.504
35	9	−1.508
40	8	−1.513
45	6	−1.521

TABLE A-17: EXPERIMENTAL DATA AT 298 K AND 11.25 pH

$[DEA] = 0.097$ M, $[CO_2] = 0.0053$ M, $[Ind] = 2.5 \times 10^{-5}$ M

$V_o = 2.5$ V $V_{io} = 2.4$ V $Z = 0.001$

Run C-17

Time (Milli sec.)	Graduations	Log D_t
5	24	-1.451
10	20	-1.466
15	16	-1.481
20	14	-1.489
25	12.5	-1.494
30	10	-1.504
35	9	-1.508
40	8	-1.513
45	6	-1.521
50	5	-1.525

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